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LETTERS TO THE EDITOR

Reaction of 2-Propynyl Acetate and 1,1-dimethyl-2-propynyl Chloroacetate with Amines

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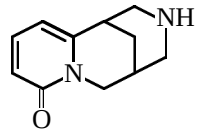
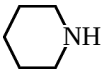
Polyfunctional acetylenic aminoesters exhibit a broad-spectum biological activity due to the precence of several receptor-binding centers [1, 2]. To find the most active pharmacotropic fragments, we synthesized a series of new complex acetylenic aminoesters which are also intersting synthons for further transformations. We established that the aminoesters are most convenient to prepare by reactions of 2-propynyl acetates and 1,1-dimethyl-2-propynyl chloroacetate with amines.

$$RH + ClH_2C(O)OCR'C{\equiv}CH \longrightarrow RCH_2C(O)OCR'C{\equiv}CH,$$

Ia, Ib–VIa, VIb

RH =  (**I**),  (**II**),

$(C_2H_5)_2NH$ (**III**),  (**IV**), R' = H_2 (**a**), $(CH_3)_2$ (**b**).

The structure of products **Ia, Ib–IVa, IVb** was proved by ^{1}H NMR and IR spectroscopy, and elemental analysis. The IR spectra contain absorption bands characteristic C≡C (2110–1130 cm^{-1}) and C=O groups (1740–1765 cm^{-1}). In the ^{1}H NMR spectra of **Ia, Ib–IVa, IVb**, the C≡CH proton signal is at 3.5–4.2 ppm.

2-Propynyl cytisinoacetate (Ia). To a solution of 1.3 g of cytisine in benzene we added 0.71 g of triethylamine and then, dropwise with stirring, 0.93 g of 2-propynyl chloroacetate, after which the mixture was stirred with heating with a reflux condenser for 5 h. After filtration and removal of the solvent, the thick oily residue crystallized. Yield 1.5 g (76%), mp 74–75°C. Found, %: C 68.3; H 6.15; N 9.7. $C_{16}H_{18}NO_3$. Calculated, %: C 67.13; H 6.3; N 9.8.

Compounds **IIa–VIa** and **Ib–VIb** were prepared in a similar way.

2-Propynyl morpholinoacetate (IIa). Colorless crystals. Yield 63%, mp 45–46°C. Found, %: C 59.09; H 4.96; N 7.89. $C_9H_9NO_3$. Calculated, %: C 59.14; H 4.93; N 7.67.

2-Propynyl diethylaminoacetate (IIIa). Light yellow oil. Yield 70%, bp 62–63°C (5 mm). Found, %: C 63.98; H 8.93; N 8.25. $C_9H_{15}NO_2$. Calculated, %: C 64.04; H 8.89; N 8.30.

2-Propynyl piperidinoacetate (IVa). Light oil. Yield 66%, mp 92–93°C (5 mm). Found, %: C 66.36; H 5.71; N 7.79. $C_{10}H_{10}NO_2$. Calculated, %:C 66.42; H 5.53; N 7.75.

1,1-Dimethyl-2-propynyl cytisinoacetate (Ib). Thick colorless oil. Yield 65%. Found, %: C 68.9; H 7.2; N 8.3. $C_{18}H_{22}N_2O_3$. Calculated, %: C 68.78; H 7.0; N 8.9.

1,1-Dimethyl-2-propynyl morpholinoacetate (IIb). Light yellow oil. Yield 57%, bp 100–102°C (5 mm). Found, %: C 62.91; H 5.97; N 6.74. $C_{11}H_{13} \cdot NO_3$. Calculated, %: C 62.67; H 6.17; N 6.65.

The IR spectra were recorded on a UR-20 instrument (KBr). The NMR spectra were measured on a Varian Mercury-300 spectrometer (300 MHz), solvent $CDCl_3$, internal reference HMDS.

REFERENCES

1. CH Patent 669 192, 1989, *Ref. Zh. Khim.*, 1990, 11046P.
2. US Patent 4 301 158, 1981, *Ref. Zh. Khim.*, 1982, 1 803 42P.

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